



Short communication

The application of spray drying method in valve-regulated lead-acid battery

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HIGHLIGHTS

- Spray drying method has been applied to the field of lead-acid batteries.
- Lead powder/carbon black composite was obtained by spray drying and subsequent calcination process.
- The sum of discharge capacity was increased by 8.27%.
- The charge acceptance of the test cell also can be obviously enhanced.

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ABSTRACT

Spray drying method has been successfully applied to the field of lead-acid batteries. Lead powder/carbon black composite can be obtained by spray drying and subsequent calcination process. Glucose is added to increase the adhesion of carbon black and lead powder. The morphology changes before and after calcination are examined by FE-SEM. The composite negative material can enable the sum of discharge capacity increased by 8.27% from 4374.855 Ah to 4736.706 Ah at a discharge current of 25 A after 66 cycles. And the charge acceptance of the test cell also can be obviously enhanced.

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1. Introduction

In 1997, M. Shiomi reported that carbon could form a conductive network on PbSO₄ particles of the discharged negative plates, and increased amount of carbon in the negative plates of valve-regulated lead-acid batteries could reduce the PbSO₄ accumulation and extend the life performance [1]. Especially in recent years, in order to meet the needs of various types of hybrid electric vehicles (HEV), many kinds of carbon materials such as carbon black, graphite, activated carbon etc. have been mixed in the negative active material (NAM) to improve the performance of lead-acid batteries [2–5]. Now, it has been widely accepted that carbon can effectively reduce lead sulfate accumulation under high-rate partial-state-of-charge working conditions for HEV. In addition, carbon can also enhance the conductivity of NAM and improve battery charge acceptance [6,7]. Moreover, D. Pavlov et al. discovered that charge transfer resistance on the Pb/H₂SO₄

interface is higher than that on the EAC (electrochemically active carbon)/H₂SO₄ interface [4]. Therefore, carbon added to the negative plate acts as electrocatalyst to the charge reaction. From the previous reports, it can be concluded that carbon plays a critical role in the performance of lead-acid batteries, although its addition amount is usually less than 2.0%. The traditional paste mixing technology is mechanical agitation, which is difficult to uniformly mix carbon and lead powder. Therefore, it is necessary to seek a new way to improve the uniformity degree. If the contact area of the carbon and active material is increased, this will have a great impact on battery performance. In X. He's report, it has been approved that if the contact between the LiFePO₄ and carbon black is improved by dispersion agent, the discharge capacities will be 121.4 mAh g^{−1} (1C), 104.0 mAh g^{−1} (3C) and 92.0 mAh g^{−1} (5C) and 3.3 mAh g^{−1} (1C), 6.3 mAh g^{−1} (3C) and 10.3 mAh g^{−1} (5C) more than the other electrode, respectively [8].

Spray drying method has been widely used in the preparation of lithium-ion battery electrode materials. Recently, Liu et al. prepared LiFePO₄/graphene and SnO₂/graphene composites using spray drying method, respectively [9,10]. When used as an electrode

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material for lithium-ion batteries, the composites presented excellent rate capability and cyclic stability. Spray drying method not only can uniformly mix the raw materials but also makes the mixture to form granules. Graphene in the electrode materials forms a three-dimensional conductive network, which will facilitate electron migration. Here, according to the material properties of lead-acid batteries, we make some adjustments and improvements on the technology and promote the use of spray drying method to the field of lead-acid batteries.

2. Experimental

2.1. Preparation of lead powder/carbon black composite

10 kg lead powder with oxidation degree of 77.5%, 100 g carbon black (Cabot Vulcan XC72R) and 200 g glucose were added into a mixture of 50 kg water–ethanol (volume ratio 9:1) in an agitated tank. Then, the slurry was vigorously stirred and spray dried at 200 °C. Thereafter, a solid lead powder/carbon black composite was collected. The composites were heated to 300 °C at a rate of 10 °C min⁻¹ and annealed at that temperature for 3 h under N₂.

2.2. Characterizations

The X-ray powder diffraction (XRD) patterns of lead powder/carbon black composite were characterized on a Bruker D8 advanced X-ray diffractometer equipped with graphite-monochromatized Cu K α radiation ($K\alpha = 1.5418 \text{ \AA}$). The scanning electron microscopy (SEM) images were taken by a JEOL JSM-7600F field emission instrument.

2.3. Negative plate preparation

The negative pastes were prepared using lead powder/carbon black composite, H₂SO₄ (1.4 sp. gr.) 9.7%, Vanisperse A 0.2% and

BaSO₄ 0.8%. The grids were casted from Pb–Ca–Sn alloy. Their dimensions were 150 mm $\times$ 149 mm $\times$ 1.5 mm.

2.4. Test cell design

The influence of spray drying method on the performance of lead-acid cells was investigated using 2 V 100 Ah cells with 7 negative and 6 positive plates per cell. The positive plates were fabricated by Shandong Sacred Sun Power Sources Industry Co. Ltd. AGM separators with a thickness of 2.4 mm were used at 22% compression. The cells were finally filled with a sulfuric acid solution of 1.245 g cm⁻³ density. A reference cell was assembled in which negative paste was prepared by traditional mechanical stirring.

2.5. Cycling life test

Two cells were selected from the test cells and reference cells after container formation, respectively. Subsequently, the cells were assigned to perform the cycling life test on Digatron BTS-600 according to the following procedure: charge with 15 A, 2.4 V for 16 h, 2 min stand, discharge with 25 A constant current, when the cell voltage fell down to 1.8 V another cycle began. When the discharge capacity of test cells was less than 60 Ah (60% of rated capacity), the cycling life test was stopped.

2.6. Charge acceptance test

This type 2 V 100 Ah battery is designed for energy storage. Therefore, the charge acceptance of test cell and reference cell were examined according to GB/T 22473-2008 [11]. The batteries were discharged at a temperature of 25 °C and at a current $I_0 = C_e/10$ for 5 h, where C_e was taken as the maximum value of the three C_{10} initial capacity check. After discharge, the batteries were cooled at 0 °C for 24 h. Thereafter, at this temperature of 0 °C, the batteries



Fig. 1. The color change before and after spray drying.

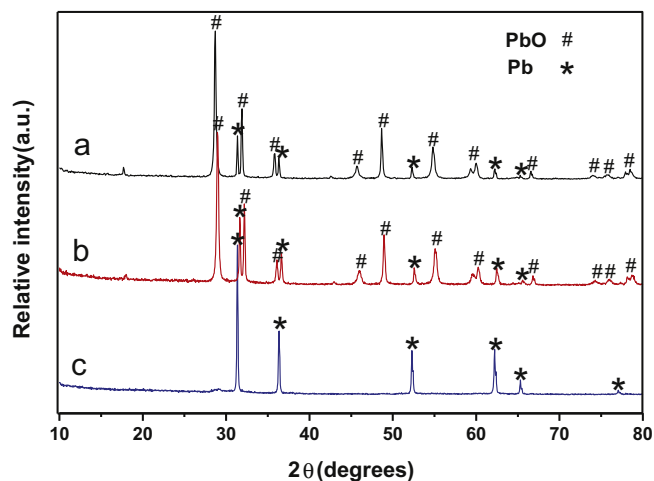


Fig. 2. XRD patterns of the samples before calcination (a), after calcined at 300 °C (b) and 400 °C (c).

were charged at a constant voltage of 2.4 V. The charging current was recorded at 1 min intervals and I_{ca} was recorded after 10 min. The ratio i_{ca} of I_{ca} to $C_{10}/10$ was calculated.

3. Results and discussion

Obvious color change can be seen in Fig. 1. Brownish yellow lead powder and carbon black were treated by spray drying process, and the color of mixed powder became gray. Furthermore, according to the color uniformity of mixed powders, it can be deduced that lead powder and carbon black were fully well-mixed. Compared with traditional mechanical agitation, spray drying can fully open the agglomeration of lead powder and carbon black, therefore the contact area between lead powder and carbon black was markedly

increased. This was helpful to form the conductive network in the negative plate.

In order to increase the adhesion of carbon black and lead powder, glucose was added in the spray drying process. But during the paste mixing process glucose would react with sulfuric acid to produce water, which led to the increased amount of sulfuric acid, and the most serious problem was that the paste was too thin and could not be coated onto the plate. Thereby, in order to eliminate adverse influence and prevent the change of lead powder oxidation degree, the mixed powder was calcined in N_2 atmosphere. The calcination temperature is also important, because the lead powder will be deoxidized at the higher temperature. At the same time, the selected temperature should ensure glucose carbonization. Fig. 2a shows the XRD pattern of mixed powder before calcination. The reflection peaks indicate that the mixed powders were mainly composed of PbO and Pb. After the mixed powders were calcined at 300 °C for 3 h, the black composite was obtained and its XRD pattern shown in Fig. 2b is almost the same as that in Fig. 2a. The analysis results imply that the calcination conditions are proper. When the calcination temperature was increased to 400 °C and maintained for 3 h, PbO was completely deoxidized and only the characteristic peaks of Pb (Fig. 2c) can be observed.

The FE-SEM images of the samples before and after calcined at 300 °C are shown in Fig. 3. It can be seen from Fig. 3a that the powders before calcination are mainly composed of quasi-spherical microparticles with diameters of 2–5 μm . The SEM image with a higher magnification (Fig. 3b) reveals that each microsphere is actually a random aggregate of lead powders and carbon black owing to the adhesion effect of glucose. As compared to Fig. 3a, the morphological changes can be distinctly observed in Fig. 3c. The structure of some quasi-spherical microparticles collapses after calcination. And a large number of smaller spherical particles emerge, which can be ascribed to the influence of temperature on the lead powder particles (melting point of Pb is 327 °C). Moreover the particles tend to be connected due to the glucose carbonization.

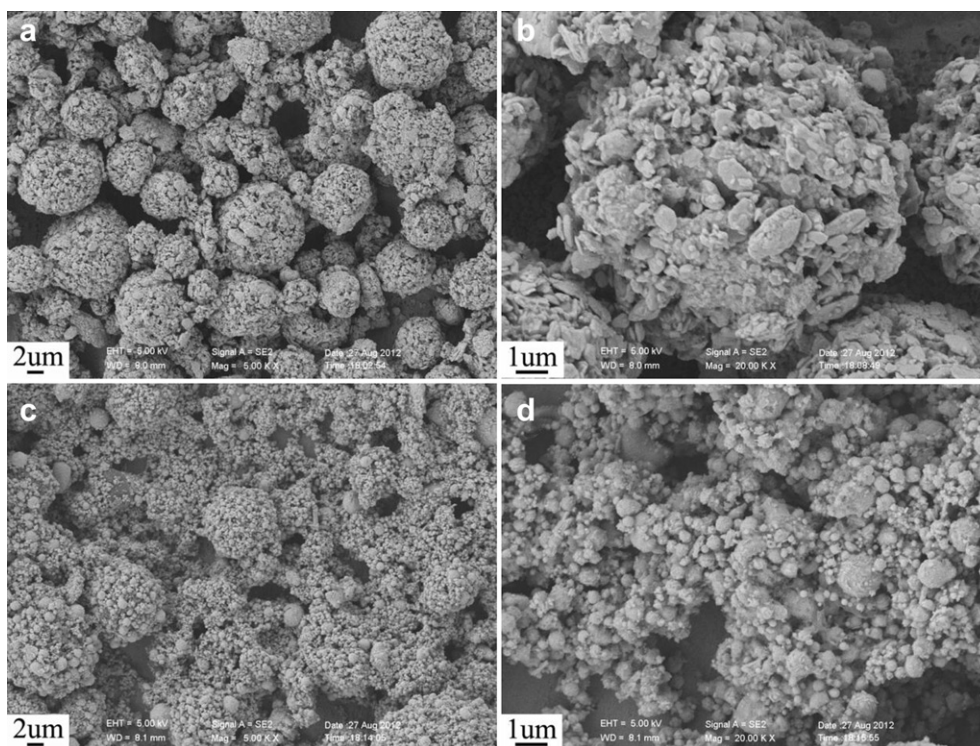


Fig. 3. SEM images of the samples before calcinations (a, b) and after calcined at 300 °C (c, d).

In order to determine the influence of spray drying and calcination, the oxidation degree of samples was detected. Before spray drying the oxidation degree of lead powder was 77.5%. After spray drying the oxidation degree was increased to 81.5%, because the warm and humid environment can accelerate the oxidation of lead powder in the spray drying process. However, the value of oxidation degree was reduced to 76.6% after calcined at 300 °C owing to the weak deoxidization capability of glucose. The value of oxidation degree after calcination is close to that before spray drying, which means that the calcined lead powder was suitable for fabricating batteries.

After the formation, the cells were executed C_{10} initial capacity measurements. The initial capacity of test cell is 99.8 Ah at the third C_{10} capacity test which is very close to the rated capacity value. And this value is a little lower than that of the reference cell, which can reach 106.5 Ah at the first C_{10} capacity test. Our experimental results are similar to the former reports [4].

In Fig. 4a, it can be seen that the cycle curves have the similar trend. Whereas the discharge capacity plateau of test cell is obviously higher than the reference cell, suggesting the test cell can store–release more energy. It can be calculated that the spray drying method will enable the sum of discharge capacity increased by 8.27% from 4374.855 Ah to 4736.706 Ah at a discharge current of

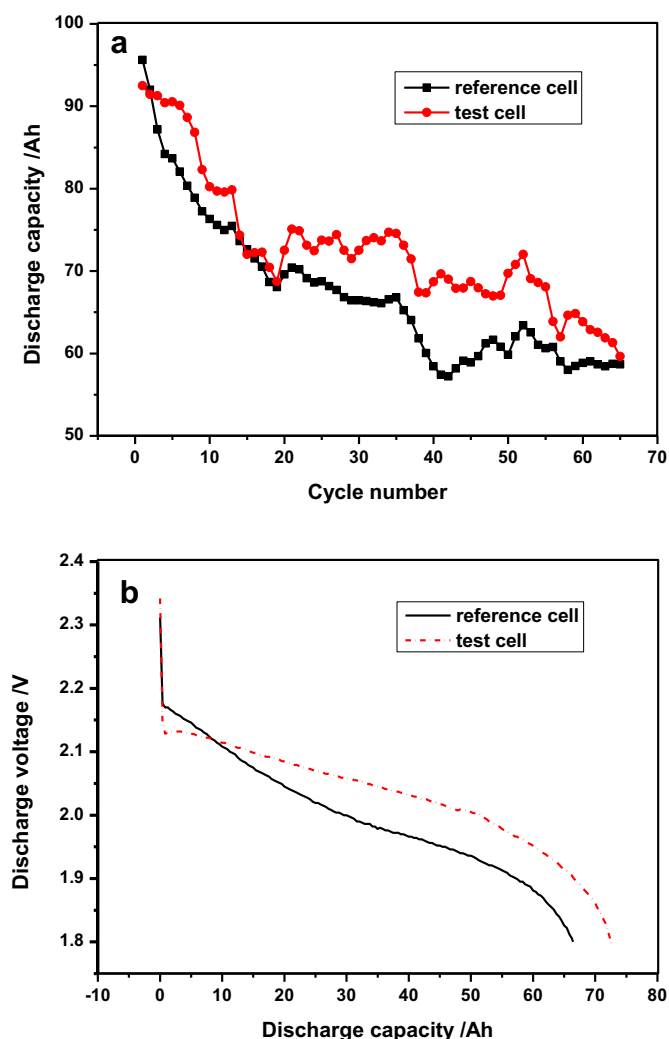


Fig. 4. (a) Comparative cycling performances and (b) the 30th cycle discharge voltage curve of test cell and reference cell, respectively.

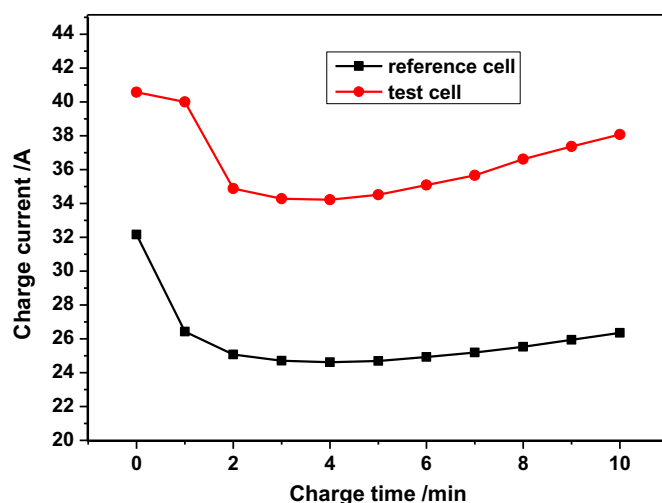


Fig. 5. The charge acceptance curves of test cell and reference cell, respectively.

25 A after 66 cycles. The 30th cycle was chosen as a typical cycle to study the changes of discharge voltage. As shown in Fig. 4b, the initial discharge voltage of the test cell is 30 mV lower than that of the reference cell due to the higher ohmic resistance coming from excessive carbon. However, after discharging 8.749 Ah, the discharge voltage plateau of the test cell is markedly higher than the reference cell. With the increase of discharge time, the lead active materials have been gradually oxidized to nonconductive $PbSO_4$. At this time, the carbon black added by spray drying method will be more helpful to reduce the cell resistance. Uniformly dispersed carbon black can not only effectively increase the electrochemically active surface of the NAM [4] but also be easier to form conductive network in the NAM [1].

After failure on cycling, the values of electrolyte density were 1.3181 and 1.3441 $g\ cm^{-3}$ for the reference cell and test cell, respectively. However, the values of electrolyte density after formation were 1.3168 and 1.3180 $g\ cm^{-3}$ for reference cell and test cell, respectively. From the changes of electrolyte density, it can be concluded that dehydration almost does not occur in the reference cell, but a certain degree of dehydration must happen in the test cell because of the existence of more carbon. In fact, overheating phenomenon does not appear in the test cell, because the dehydration process is very slow and does not influence the cycling life test.

The charge acceptance curves of test cell and reference cell are shown in Fig. 5. It can be seen that the charge current curve of test cell is obviously higher than that of reference cell. The C_e values of test cell and reference cell were 102.5 Ah and 108.5 Ah. And the values of I_{ca} were recorded as 38.08 A for test cell and 26.36 A for reference cell. Thereby, the ratio i_{ca} can be calculated as 3.808 and 2.636, respectively. These two values are both greater than the standard value of 2. The above test results indicate that the charge acceptance of test cell is distinctly better than that of reference cell.

4. Conclusions

Our experiments prove that the spray drying is a very effective raw materials mixing method and it can be applied to mix lead powder and other expander components. This method will lead the cell to sacrifice some of the initial capacity, but at the same time it will help the cell to store and release more energy in the cycling

process. In addition, it is especially important that the spray drying technology provides a new idea for the development of high-performance lead-acid batteries. Moreover, this technology is easy to achieve large-scale production. However, in fact it still is a challenge to explore its practical application in the manufacture of lead-acid batteries. Thereby, further studies are needed to simplify the experimental process, decrease the preparation cost, increase the discharge capacity and enhance the cycling capability. At present, more researches on this aspect are underway.

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References

- [1] M. Shiomi, T. Funato, K. Nakamura, K. Takahashi, M. Tsubota, J. Power Sources 64 (1997) 147–152.
- [2] M. Fernández, J. Valenciano, F. Trinidad, N. Muñoz, J. Power Sources 195 (2010) 4458–4469.
- [3] P. Bača, K. Micka, P. Krivík, K. Tonar, P. Tošer, J. Power Sources 196 (2011) 3988–3992.
- [4] D. Pavlov, T. Rogachev, P. Nikolov, G. Petkova, J. Power Sources 191 (2009) 58–75.
- [5] D. Pavlov, P. Nikolov, T. Rogachev, J. Power Sources 196 (2011) 5155–5167.
- [6] K. Nakamura, M. Shiomi, K. Takahashi, M. Tsubota, J. Power Sources 59 (1996) 153–157.
- [7] P.T. Moseley, J. Power Sources 191 (2009) 134–138.
- [8] W. Zhang, X. He, W. Pu, J. Li, C. Wan, Ionics 17 (2011) 473–477.
- [9] X.F. Zhou, F. Wang, Y.M. Zhu, Z.P. Liu, J. Mater. Chem. 21 (2011) 3353–3358.
- [10] X.Y. Wang, X.F. Zhou, K. Yao, J.G. Zhang, Z.P. Liu, Carbon 49 (2011) 133–139.
- [11] GB/T 22473–2008, Lead-acid Storage Batteries Used for Energy Storage, Standardization Administration of China, Beijing, 2009.